iodine vapour referred to above, that the molecular constitution of the iodine vapour at these higher temperatures is in all probability different from what it is at ordinary room temperatures. It might, therefore, happen that the molecules of the heated iodine vapour would not be stimulated to emission at all by the light from the green and the yellow lines of the mercury arc spectrum. If this were so, the lines in the Wood spectrum could not then appear on the plates. At the same time, it might be possible that the molecules of the heated vapour would respond to a stimulation by the light from a line or lines in the ultra-violet portion of the mercury arc spectrum. If such a stimulation had the effect of causing the heated vapour to emit a fluorescence spectrum, the light constituting this spectrum might easily pass through the cold vapour without any absorption and so give rise to the bands obtained in the present investigation.

In conclusion, I wish to acknowledge the services of my assistants, F. Mezen and P. Blackman, the one in quartz-blowing and the other in preliminary work on the photographs.

The Abnormal Kinetic Energy of an Ion in a Gas.

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(Communicated by Prof. J. S. Townsend, F.R.S. Received and read March 13, 1913.)

1. In a paper on "The Charges on Ions in Gases, and the Effect of Water Vapour on the Motion of Negative Ions," Townsend* showed that when a stream of ions is moving in an electric field the extent to which it spreads out as it advances depends on the dryness of the gas as well as on the electric force, indicating that the rate of diffusion in dry air is abnormally great in comparison with the velocity under an electric force. It was suggested (*loc. cit.*, p. 469) that this could be explained on the supposition that the ions were not in "thermal equilibrium" with the molecules of the gas, but that their mean kinetic energy exceeded that of an equal number of gas molecules in the ratio k to unity, where k depends on the pressure and the electric force. Townsend mentioned a possible means by which this abnormal energy might arise, namely, that the extra velocity acquired by an ion in an interval

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* J. S. Townsend, 'Roy. Soc. Proc.,' 1908, A, vol. 81, p. 464.

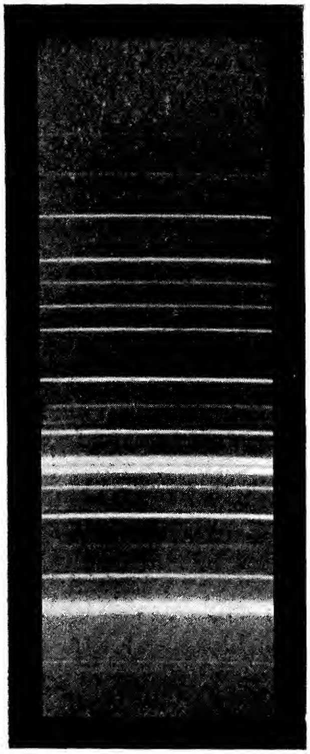

FIG. 1.

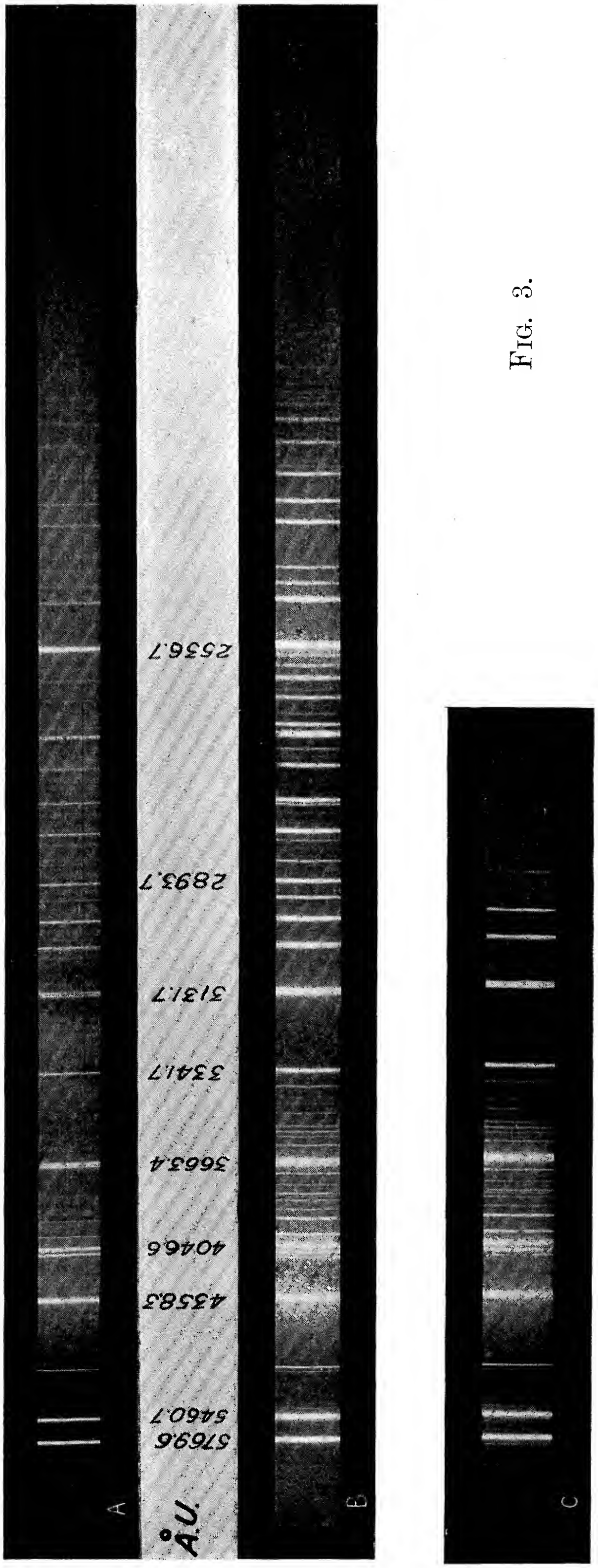
2536.7
2893.7
3131.7
3341.7
3663.4
4046.6
4358.3
5460.7
5769.6
Å.U.
A
B
C

FIG. 3.

between collisions was not all lost by collision with a gas molecule, so that energy might accumulate for some time. The effect has been further studied by Haselfoot,* both observers showing that k is, at any rate approximately, a function of X/p only, where X is the electric force and p the pressure of the gas.

It seemed to the author that it would be desirable to investigate the matter quantitatively on the basis of the kinetic theory of gases, since we are here dealing with the validity or non-validity of the law of equipartition of energy. It is shown in this paper that it is easy enough to obtain theoretical support for the assumption of abnormal kinetic energy; in fact, the values of k predicted by pure theory are considerably in excess of those actually observed. In order to prevent misunderstanding, it may be stated that the law of equipartition of energy in the kinetic theory is only proved to be true when the molecules are left to themselves in the absence of external forces.

2. The most satisfactory way of treating these questions is that developed by Maxwell† in his later papers, and carried out by him on the assumption of an inverse fifth-power law of repulsion between molecules. Where not otherwise stated we shall follow the notation used by Jeans‡ in his account of Maxwell's theory.

Let n = Number of ions per cubic centimetre of the gas, small in comparison with
N = Number of molecules of gas per cubic centimetre.
$(\mathrm{X}, \mathrm{Y}, \mathrm{Z})$ = Electric force.
θ = Absolute temperature of the gas.
(u, v, w) = Velocity of an ion.
$(u_0, v_0, w_0) = (\bar{u}, \bar{v}, \bar{w})$, the mass-velocity of a group of ions. Writing $(u, v, w) = (u_0+\mathrm{U}, v_0+\mathrm{V}, w_0+\mathrm{W})$, $(\mathrm{U}, \mathrm{V}, \mathrm{W})$ is called the velocity of agitation of an ion, so that $\bar{\mathrm{U}} = \bar{\mathrm{V}} = \bar{\mathrm{W}} = 0$.
(u', v', w') = Velocity of agitation of a gas molecule.
m, M = Mass of ion and molecule respectively.
$\alpha\theta$ = Average kinetic energy of agitation of a gas molecule.
$k\alpha\theta = \frac{1}{2}m(\overline{\mathrm{U}^2}+\overline{\mathrm{V}^2}+\overline{\mathrm{W}^2})$ = average kinetic energy of agitation of the ions in a specified small region.

$$h = 3/4\alpha\theta, \quad \lambda = \mathrm{MNK}^{\frac{1}{2}}(m+\mathrm{M})^{-\frac{3}{2}}, \quad \mathrm{T} = (m+\mathrm{M})^{\frac{1}{2}}/\mathrm{MNA_1K^{\frac{1}{2}}}.$$

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* C. E. Haselfoot, 'Roy. Soc. Proc.,' 1912, A, vol. 87, p. 350.

† J. C. Maxwell, 'Phil. Trans,' vol. 157; 'Collected Papers,' vol. 2, p. 26.

‡ 'Dynamical Theory of Gases,' Chap. XV.

Then Maxwell's general equation of transfer[*] becomes, in the case of steady motion,

$$\frac{\partial}{\partial x}(n\overline{u\mathrm{Q}})+\frac{\partial}{\partial y}(n\overline{v\mathrm{Q}})+\frac{\partial}{\partial z}(n\overline{w\mathrm{Q}}) = \frac{ne}{m}\left[\mathrm{X}\left(\overline{\frac{\partial \mathrm{Q}}{\partial u}}\right)+\mathrm{Y}\left(\overline{\frac{\partial \mathrm{Q}}{\partial v}}\right)+\mathrm{Z}\left(\overline{\frac{\partial \mathrm{Q}}{\partial w}}\right)\right]+\Delta \mathrm{Q}. \tag{1}$$

The equation of continuity is

$$\frac{\partial}{\partial x}(nu_0)+\frac{\partial}{\partial y}(nv_0)+\frac{\partial}{\partial z}(nw_0) = 0. \tag{2}$$

Putting $\mathrm{Q} = u, v, w$ in succession gives the three well-known equations of the type

$$\frac{\partial}{\partial x}(n\overline{u^2})+\frac{\partial}{\partial y}(n\overline{uv})+\frac{\partial}{\partial z}(n\overline{uw}) = \frac{ne\mathrm{X}}{m}+\Delta u. \tag{3}$$

Putting $\mathrm{Q} = u^2$, we have

$$\frac{\partial}{\partial x}(n\overline{u^3})+\frac{\partial}{\partial y}(n\overline{u^2v})+\frac{\partial}{\partial z}(n\overline{u^2w}) = \frac{2ne\mathrm{X}u_0}{m}+\Delta u^2, \tag{4}$$

and, similarly,

$$\frac{\partial}{\partial x}(n\overline{u^2v})+\frac{\partial}{\partial y}(n\overline{uv^2})+\frac{\partial}{\partial z}(n\overline{uvw}) = \frac{ne}{m}(\mathrm{X}v_0+\mathrm{Y}u_0)+\Delta uv. \tag{5}$$

The quantities denoted by $\Delta\mathrm{Q}$, which represent the effect of collisions on Q, are calculated by Maxwell,[†] the assumption of the inverse fifth-power law now entering for the first time. In the present notation the results are

$$\Delta u = -nu_0/\mathrm{T}, \tag{6}$$

$$\Delta u^2 = -\lambda n\left\{2\mathrm{A}_1(m\overline{u^2}-\tfrac{2}{3}\alpha\theta)+\mathrm{A}_2\mathrm{M}(2\overline{u^2}-\overline{v^2}-\overline{w^2})\right\}, \tag{7}$$

$$\Delta uv = -\lambda n(2\mathrm{A}_1m+3\mathrm{A}_2\mathrm{M})\overline{uv}. \tag{8}$$

3. The immediate problem with which we are concerned is to find the kinetic energy in a stream of ions advancing in a fixed direction, for example the axis of x, the motion depending on the co-ordinate x alone. Then

$$nu_0 = \text{constant}, \tag{9}$$

$$d(mn\overline{u^2})/dx = ne\mathrm{X}-mnu_0/\mathrm{T}, \tag{10}$$

$$d(mn\overline{u^3})/dx = 2ne\mathrm{X}u_0-\lambda mn\left\{(2\mathrm{A}_1m+3\mathrm{A}_2\mathrm{M})\overline{\mathrm{U}^2}-\tfrac{4}{3}\mathrm{A}_1\alpha\theta-2\mathrm{A}_2\mathrm{M}k\alpha\theta/m \right.$$
$$\left. +(2\mathrm{A}_1m+2\mathrm{A}_2\mathrm{M})u_0^2\right\}, \tag{11}$$

$$d(mn\overline{uv^2})/dx = -\lambda mn\left\{(2\mathrm{A}_1m+3\mathrm{A}_2\mathrm{M})\overline{\mathrm{V}^2}-\tfrac{4}{3}\mathrm{A}_1\alpha\theta-2\mathrm{A}_2\mathrm{M}k\alpha\theta/m \right.$$
$$\left. -\mathrm{A}_2\mathrm{M}u_0^2\right\}, \tag{12}$$

$$d(mn\overline{uw^2})/dx = -\lambda mn\left\{(2\mathrm{A}_1m+3\mathrm{A}_2\mathrm{M})\overline{\mathrm{W}^2}-\tfrac{4}{3}\mathrm{A}_1\alpha\theta-2\mathrm{A}_2\mathrm{M}k\alpha\theta/m \right.$$
$$\left. -\mathrm{A}_2\mathrm{M}u_0^2\right\}. \tag{13}$$

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[*] Jeans, p. 277.

[†] 'Collected Papers,' vol. 2, pp. 47–48.

Here k may be a function of x, and the equations will apply to the motion of a stream of ions advancing with gradual rise of kinetic energy. It is natural to inquire whether there is any final state towards which the motion tends when the stream has travelled some distance. In this case the d/dx terms vanish, and (10) gives

$$u_0 = e\mathrm{XT}/m. \tag{14}$$

Substituting for X from this equation in (11), (12), and (13), we find

$$\left.\begin{aligned}(2\mathrm{A}_1 m+3\mathrm{A}_2\mathrm{M})\overline{\mathrm{U}^2} &= \tfrac{4}{3}\mathrm{A}_1\alpha\theta+2\mathrm{A}_2\mathrm{M}k\alpha\theta/m+2(\mathrm{A}_1-\mathrm{A}_2)\mathrm{M}u_0^2,\\ (2\mathrm{A}_1 m+3\mathrm{A}_2\mathrm{M})\overline{\mathrm{V}^2} = (2\mathrm{A}_1 m+3\mathrm{A}_2\mathrm{M})\overline{\mathrm{W}^2} &= \tfrac{4}{3}\mathrm{A}_1\alpha\theta+2\mathrm{A}_2\mathrm{M}k\alpha\theta/m+\mathrm{A}_2\mathrm{M}u_0^2.\end{aligned}\right\} \tag{15}$$

These latter equations yield on addition

$$k-1 = \mathrm{M}u_0^2/2\alpha\theta; \tag{16}$$

or, if Ω is the "root-mean-square value" of the velocity of agitation of the gas molecules,

$$k-1 = u_0^2/\Omega^2. \tag{17}$$

4. The inverse fifth power law has the advantage of allowing a perfectly rigorous solution of the present problem, free from all considerations of approximation. As, however, the formula (17) is not in agreement with experiment it is desirable to consider another law of force, namely, that both ion and molecule are elastic spheres. Some useful information is given by equations (15) as to the distribution of velocities of agitation in various directions. In general $\overline{\mathrm{U}^2}$, $\overline{\mathrm{V}^2}$, and $\overline{\mathrm{W}^2}$ are unequal, and their differences are of the order of magnitude of u_0^2. In two cases, however, the differences are small in comparison with the absolute value of any of the quantities; namely, when k is nearly unity, and when m is small in comparison with M. We shall, therefore, not be far wrong in assuming Maxwell's law of distribution as a first approximation.

Let f_1 (U, V, W) $d\mathrm{U}\,d\mathrm{V}\,d\mathrm{W}$ represent the fraction of the whole number of ions which have velocities of agitation in the range (U, V, W) and (U + dU, V + dV, W + dW): then Maxwell's law is expressed by

$$f_1 = (hm/k\pi)^{3/2}e^{-hm(\mathrm{U}^2+\mathrm{V}^2+\mathrm{W}^2)/k}. \tag{18}$$

There is no doubt as to the corresponding function $f_2(u', v', w')$ for the molecules of the gas, namely,

$$f_2 = (h\mathrm{M}/\pi)^{3/2}\,e^{-h\mathrm{M}(u'^2+v'^2+w'^2)}.$$

We shall suppose for the sake of generality that the collision of ion and molecule is not perfectly elastic, an assumption which allows roughly for a possible loss of energy on collision, though it renders the validity of (18) more doubtful than it might otherwise be. Under these conditions the calculation of ΔQ is reduced to that of certain multiple integrals.* Neglecting terms in u_0^2 as a first approximation, and taking m as small in comparison with M, we find

$$\Delta u = -\tfrac{8}{3} n N \sigma^2 u_0 f (\pi k / hm)^{\frac{1}{2}},$$

where σ is the molecular radius, and f stands for $\frac{1}{2}(1+e)$, e being the coefficient of restitution. Hence

$$u_0 = \frac{3eX}{16N\sigma^2 f}\left(\frac{3}{\pi m k \alpha \theta}\right)^{\frac{1}{2}}, \tag{19}$$

a result which for $f = k = 1$ agrees with one found by Langevin.†

In determining $k-1$, which is of the nature of a second order approximation, we have to consider the correction to be applied to the Maxwellian formula (18). It would be exceedingly difficult to determine the form of the function f_1 with rigour, although Boltzmann‡ has given an equation satisfied by it; hence it is most natural to assume a formula of the type

$$f_1 = (p + qU^2)\, e^{-\nu(U^2+V^2+W^2)}, \tag{20}$$

in which q is a small quantity of the order u_0^2. Its presence enables us to satisfy the equation $\Delta v^2 = 0$, which would remain unsatisfied on a pure Maxwellian law. We approximate to the second order in u_0 and eliminate q from the equations $\Delta u^2 = -2neXu_0/m$ and $\Delta v^2 = 0$, afterwards replacing p by $(hm/k\pi)^{3/2}$ and ν by hm/k. A somewhat tedious calculation on these lines yields the result

$$k - f + \frac{kM}{m}(1-f) = \frac{u_0^2}{\Omega^2}\,\frac{4f-3}{2-f}. \tag{21}$$

In this formula we have neglected m in comparison with M, except in the important term $kM(1-f)/m$. When the collision is perfectly elastic $f = 1$ and

$$k - 1 = u_0^2/\Omega^2,$$

exactly as in equation (17).

5. We have now to consider the equations (17) and (21) in the light of recent experiments.§ Taking $\Omega^2 = 2{\cdot}5 \times 10^9$ for air at 15° C., the following table gives the kind of results obtained.

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* *Cf.* Jeans, 'Dynamical Theory of Gases,' equation (685), p. 289.

† P. Langevin, 'Ann. Chim. Phys.,' 1905, Ser. 8, vol. 5, p. 245; e, of course, here denotes the charge on the electron.

‡ Boltzmann, 'Gastheorie,' vol. 1, p. 114 (contains some obvious misprints).

§ J. S. Townsend and H. T. Tizard, 'Roy. Soc. Proc.,' 1913, A; also C. E. Haselfoot, *loc. cit.*

X/p ……	0·2	0·5	1	2	5	10	20	50	100	150
$u_0/10^5$ …………	5	9	12·5	17·5	30	52	90	173	270	350
$k-1$ (observed)	1·8	4·5	9	20	35	44	55	100	160	210
$k-1$ from (17)	100	320	630	1200	3600	$1·1 \times 10^4$	$3·2 \times 10^4$	$1·2 \times 10^5$	$2·9 \times 10^5$	$4·9 \times 10^5$

The theoretical values are thus much too high throughout, particularly at the larger electric forces.

The source of the discrepancy might be sought in the remark that the final state here contemplated was not attained in the experiments of Townsend and Tizard; but though there is some theoretical support for this view it would lead to the conclusion that the observed values of k are not functions of X/p only, and is thus negatived by experiment. The equation (21), however, taken in a wide enough sense, is capable of explaining the discrepancy. If f is less than unity there is a loss of energy on impact, and it appears reasonable to suppose that this loss will increase as more and more ions reach the velocity necessary to form other ions by collision. In fact, we calculate the quantity f as a function of X/p by means of equation (21), using the observed values of u_0 and k. Since M/m has the value $5·3 \times 10^4$, a very slight defect of f from unity will cause a great drop in the value of k, while leaving the formula (19) for the mobility practically unaltered. The coefficient of restitution e, here viewed in a somewhat wider sense, may be called the energy coefficient; and we may say roughly that the loss of energy on collision under a given electric force is on the average that of an imperfectly elastic impact with the corresponding value of e. The results of the calculation are:—

X/p……	0·2	0·5	1	2	5	10	20	50	100	150
Energy coefficient e	0·9986	0·9976	0·9975	0·9976	0·996	0·99	0·98	0·95	0·93	0·92

The formula (21) cannot be pushed to extremes. It is clearly erroneous when f is less than $\frac{3}{4}$, *i.e.* when e is less than $\frac{1}{2}$; but the formula (20) becomes less and less applicable at high speeds, and would probably fail before e sank to this value. As, however, (21) reduces to the exact formula (17) when $f = 1$ it may be regarded as a reasonable generalisation to cover the case of loss of energy by collision.

It is of interest to calculate the ratio of the velocity of drift u_0 to the velocity of agitation ω of the ions themselves. Since $m\omega^2 = k\mathrm{M}\Omega^2$ we have from (21)

$$\frac{u_0^2}{\omega^2} = \frac{2-f}{4f-3}\left[\frac{m}{\mathrm{M}}\frac{k-f}{k}+1-f\right]. \tag{22}$$

From the preceding numbers it is clear that u_0/ω is quite small for low values of X/p; but the ratio rises with increasing electric force, and ultimately becomes comparable with unity.* It may, of course, happen that there is no steady state of uniform velocity in this case.

The equation (17), though it gives values of k that are too high, applies to the case of an ion whose mass may have any ratio to that of the gas molecule. If m is comparable with M, ω is comparable with Ω. Hence unless k is very near to unity u_0 is of the order of magnitude of ω. Thus with positive ions, the mass of which is comparable with that of a molecule, we should expect the velocity of drift of the ions to approach their velocity of agitation for electric forces less than those required to produce abnormal kinetic energy. Much higher electric forces would be required, but the equation of diffusion would be seriously invalidated, and the effects observed by Townsend greatly modified. It thus appears probable that these effects are limited to negative ions.

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* If $f = 1$, $u_0^2/\omega^2 < m/\mathrm{M}$ for all values of k.

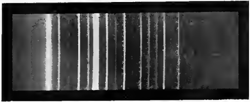

Fig. 1.

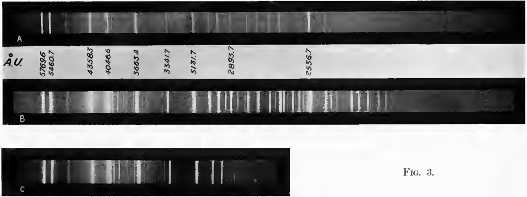
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Fig. 3.